An Improved Method for the Preparation of Bis-DiphenylPhosphino Acetylene and unsymmetrical Aryl Suhstituted Diphenylphosphino Acetylenes

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Abstract

The conventional method for preparation of bis-diphenyl phosphino acetylene (1) involves reaction of two moles of diphenyl chlorophosphine with the di Grignard of acetylene. This method gives low yields, due to impurities and moisture in the acetylene and incomplete conversion to the di Grignard. We have developed a modified procedure involving reaction of diphenylchlorophosphine with commercially available powdered sodium mono acetylide in THF, giving diphenylphosphino acetylene (2). Reaction in situ of 2 with one equivalent of n-butyl lithium in hexane gives the mono lithium adduct (3), which on treatment with a second mole of diphenyl chlorophosphine gives 1 in ~80% yields. This method avoids purifying and working with acetylene gas, and also allows greater flexibility for the synthesis of unsymmetrical bis-diaryl substituted phosphino acetylenes, by employing the above sequence with differing diaryl substituted chlorophosphines.

$$(C_6H_5)_2PCl + NaC{\equiv}CH \xrightarrow[THF]{} \underset{2}{(C_6H_5)_2PC{\equiv}CH} \xrightarrow{\text{n-butyl Li}} \underset{3}{(C_6H_5)_2PC{\equiv}C\,Li} \xrightarrow{(C_6H_5)_2PCl} \underset{1}{(C_6H_5)_2PC{\equiv}CP(C_6H_5)_2}$$

Procedure for the Preparation of Bis-Diphenylphosphino Acetylene, 1

A 5 L three neck flask, equipped with mechanical stirrer, woter candenser, calcium chlaride drying tube, "Y" tube, N_2 inlet, heating mantle and 1.0 L pressure equalized drapping funnel, was charged with 1L dry THF and 50g (1.04 mal) pawdered manosadium acetylide. The mixture was heated ta reflux with stirring and 219g (196ml, 1.0 mal) diphenylchlarophasphine was added drapwise aver ane halt haur. Refluxing was cantinued far an additianol haur ta generate manoalkyne intermediate 2, then the reoctian was caaled ta roam temperature. The drapping funnel was charged with 1000 ml (1.0 mal) af 1M n-butyl lithium in hexane, which was odded drapwise with stirring aver ane haur with na externol heating, generoting manolithium solt 3. An additianal 196 ml (1.0 mal) diphenychlarasilane was charged ta the drapping tunnel and the pat heated ta reflux. The second portian af diphenychlorasilane was added drapwise aver appraximately one halt hour, then refluxing was cantinued for an additianal haur.

The heating was then discantinued and the reaction fitted with a Cloisen heod, thermometer, woter candenser, 2 L distillate receiving flask and autlet ta a water aspiratar. The arganic salvents were remaved under water vacuum with gentle mantle heating ond the pat residue caoled ta raom temperature. 1 L water was added with stirring ta dissalve salt bypraducts, and stirring cantinued far 15 minutes. The salid crude 1 was callected by suctian filtratian, washed three times with 100 ml portians at water, and air dried avernight. Wt crude 1, 347g (88%) mp 75-80° C. Recrystallization fram benzene affarded 249g (63%) Bis-Diphenylphasphina Acetylene, 1, mp 85-7° C,

Lit: mp 86-8° C